IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Peters et al

Serial No.: 09/238,851	Examiner: Webb, G.
Filed: 1/27/99	Art Unit: 1751
Docket No.: 5545A	

Title: Low Surface Tension, Low Viscosity,Aqueous, Acidic Compositions Containing Fluoride And Organic Polar Solvents For Removal Of Photoresist And Inorganic Etch Residues At Room Temperature

DECLARATION OF R. ROVITO UNDER 37 C.F.R. §1.132

I, Roberto Rovito, declare as follows:

1.   I currently am employed by Ashland Specialty Chemical Company, a division of Ashland Inc., as a Senior Applications Engineer where I have worked since February 1, 1999.

2.   I was awarded a Bachelor of Science in Chemistry and Mathematics in 1978 from Marietta College in Ohio and a PhD. in Organic Chemistry in 1985 from Temple University in Pennsylvania. I held a post-Doctoral post from 1985-1987 at Stanford University in California.

3.   Among my responsibilities are the development of new products and testing of existing products in the semiconductor cleaning area.

4.   All of the formulations listed in Exhibit 1 were prepared and titrated in Ashland's laboratory facilities in Easton, Pennsylvania. Formulations labeled as Examples 1-5 correspond to examples 1-5 in US Patent No. 5,972,862. Examples DP-1 and DP-2 are identical except acetic acid was added to DP-2. ACT is an example of a buffered composition within the scope of the claims of the presently claimed invention. Pages 1-2

of Exhibit 1 show calculations for creating one type of buffered solution. Page 3 contains the formulations for various examples. Pages 4-13 are titration curves for the various formulations.

5. I have reviewed the contents of Exhibit 1. The results show the difference between a buffered composion (ACT) and compositions (Examples 1-5, DP1 and DP2) that do not function as buffers. Buffered solutions are those solutions that are capable of maintaining their pH at some fairly constant value even when small amounts of acid or base are added. In general, the effective range for a given buffer is about one pH unit on either side of the pk_a of the acid being used. The most effective buffer, ie., the buffer having the greatest pH range on either side of the pk_a for a given acid is prepared using a 1:1 ratio of protonated and deprotonated forms of a weak acid. An example of such a buffer is the ACT example in Exhibit 1. Simply adding an acid and its conjugate base to a formulation does not create a solution that will function as a buffer. Examples 1-5 from patent 5,972,862 show how formulations that contain both an acid and a base fail to provide a buffered system, ie the formulations cannot maintain a fairly constant pH when small amounts of a base is added. In contrast a buffered composition of the present invention "ACT" maintains a fairly constant pH up to about the addition of 10 ml of 0.1N KOH. It was postulated in a rejection of the present invention that the addition of acetic acid to a composition containing ammonium fluoride would form a buffered solution in situ. Examples DP-1 and DP-2 show that merely adding a weak acid to a formulation does not create a solution able to with stand the addition of small amounts of 0.1N KOH.

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6. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: July 15, 2003

Roberto Rovito

0307sdec312

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EXHIBIT 1

Technical description of a buffered solution

Formulations for examples 1-5, DP-1, DP-2 and ACT

Titration curves for the formulations

4

Using a Weak Acid to Create a Buffered Solution

For a weak acid: $HA \Leftrightarrow H^+ + A^-$, and the equilibrium constant is k_a

where $k_a \equiv [H^+][A^-]/[HA]$

$\log k_a = \log [H^+] + \log [A^-] - \log [HA]$

$-\log k_a = -\log [H^+] - \log [A^-] + \log [HA]$

$-\log k_a \equiv pk_a$

$-\log [H^+] \equiv pH$

hence, $pk_a = pH - \log [A^-] + \log [HA]$

and $pH = pk_a + \log [A^-] - \log [HA]$

or $pH = pk_a + \log ([A^-]/[HA])$

if $[A^-]/[HA]$ is < 1, then $pH < pk_a$

if $[A^-]/[HA] = 1$, then $pH = pk_a$

if $[A^-]/[HA]$ is > 1, then $pH > pk_a$

EXAMPLE #1

Proprionic Acid	1.00
Amm. Fl. Anhydr.	8.00
Dimethyl Formamide	40.00
TMAF 25%	20.00
EP-120A	0.10
DI Water	30.90
pH = 5.04	

EXAMPLE #2

Phthalic Anhydride	0.10
Amm. Fl. Anhydr.	8.00
TMAF 25%	20.00
EP-120A	0.10
DI Water	31.80
Formamide	40.00
pH = 5.42	

EXAMPLE #3

Isobutyric Acid	0.20	
Amm. Fl. Anhydr.	5.00	
DMAC		35.00
TMAF 25%	40.00	
EP-120A	0.10	
DI Water	19.70	
pH = 5.42		

EXAMPLE #4

Acetic Acid	0.10
Amm. Fl. Anhydr.	10.00
Dimethyl Formamide	45.00
TMBC	3.00
EP-120A	0.10
pH = 5.45	

EXAMPLE #5

Amm. Fl. Anhydr.	1.00
Dimethyl Formamide	69.00
DI Water	29.00
Boric Acid	0.30

DP1

DMAC	67.5
DI Water	30.0
NH4F (40%)	2.5
Acetic Acid (glac.)	0.0

DP 2

DMAC	65.5
DI Water	30.0
NH4F (40%)	2.5
Acetic Acid (glac.)	2.0

ACT

DMAC	57.5
Ammonium Acetate	15.6
Acetic Acid (glac.)	12.0
DI Water	12.4
Amm. Floride (40%)	2.5
pH = 4.75	

DMAC - Dimethylacetamide
TMAF - Tetramethylammonium formate
TMBF - Tetramethylammonium acetate
EP-120A - Is a poly(oxyethylene)phenylester from Dai-ichi Kogyo Seiyaku Co., Ltd.

Titration Curves for Various Formulations

pH vs. Volume of 0.1N KOH Added (ml)

Legend:
- Example 1
- Example 2
- Example 3
- Example 4
- Example 5
- DP 1
- DP 2
- ACT

EX #1 (011598)
pH/ml

```
'fr
751 GPD Titrino           09140    751.0020  titant/0.1% KOH
date  2001-03-21    time  10:38        215
card label:Appl.751
pH(init)          4.61    DET pH      NE14PA
smpl size       0.5061        id#1     EX #1
EP1             1.220 ml                6.69
stop #EP reached
device label      Titrino        sign:JE
            =============

'mp
751 GPD Titrino           09140    751.0020
date  2001-03-21    time  10:38        215
pH(init)          4.61    DET pH      NE14PA
smpl size       0.5061        id#1     EX #1
   V/ml              pH      T/øC       ERC
  0.0000            4.615               0.0
  0.0500            4.637              13.2
  0.1000            4.665              16.1
  0.1500            4.693              18.3
  0.5120            4.940              23.4
  0.8000            5.231              31.5
  0.9440            5.454              40.7
  1.0380            5.662              51.1
  1.1180            5.931              60.6
  1.1800            6.314              65.9
  1.2320            6.806              66.9
  1.2840            7.238              63.7
  1.3440            7.484              55.7
  1.3940            7.620              44.9
  1.5380            7.876              34.5
  1.7240            8.079               0.0
  1.9740            8.262               0.0
            =============
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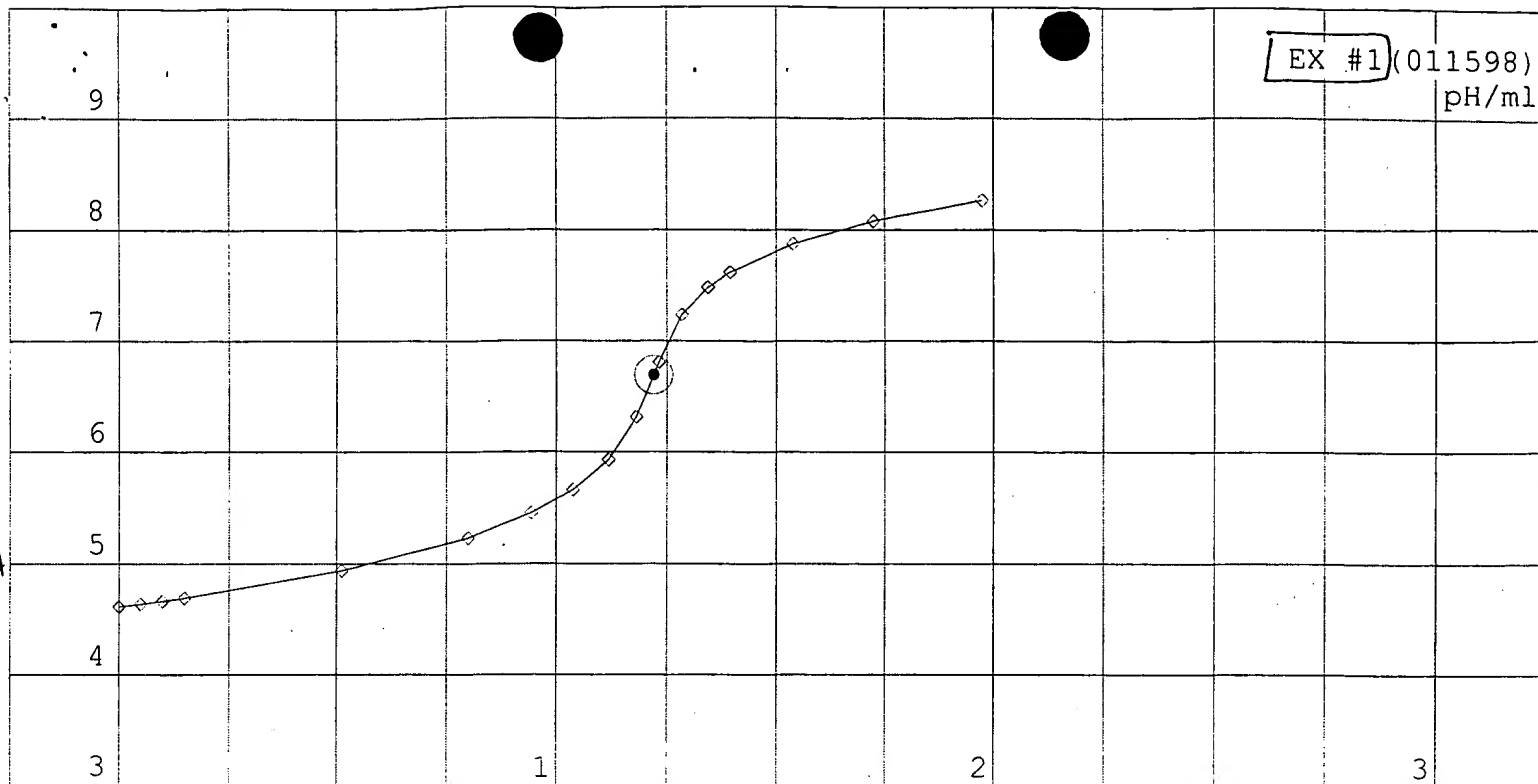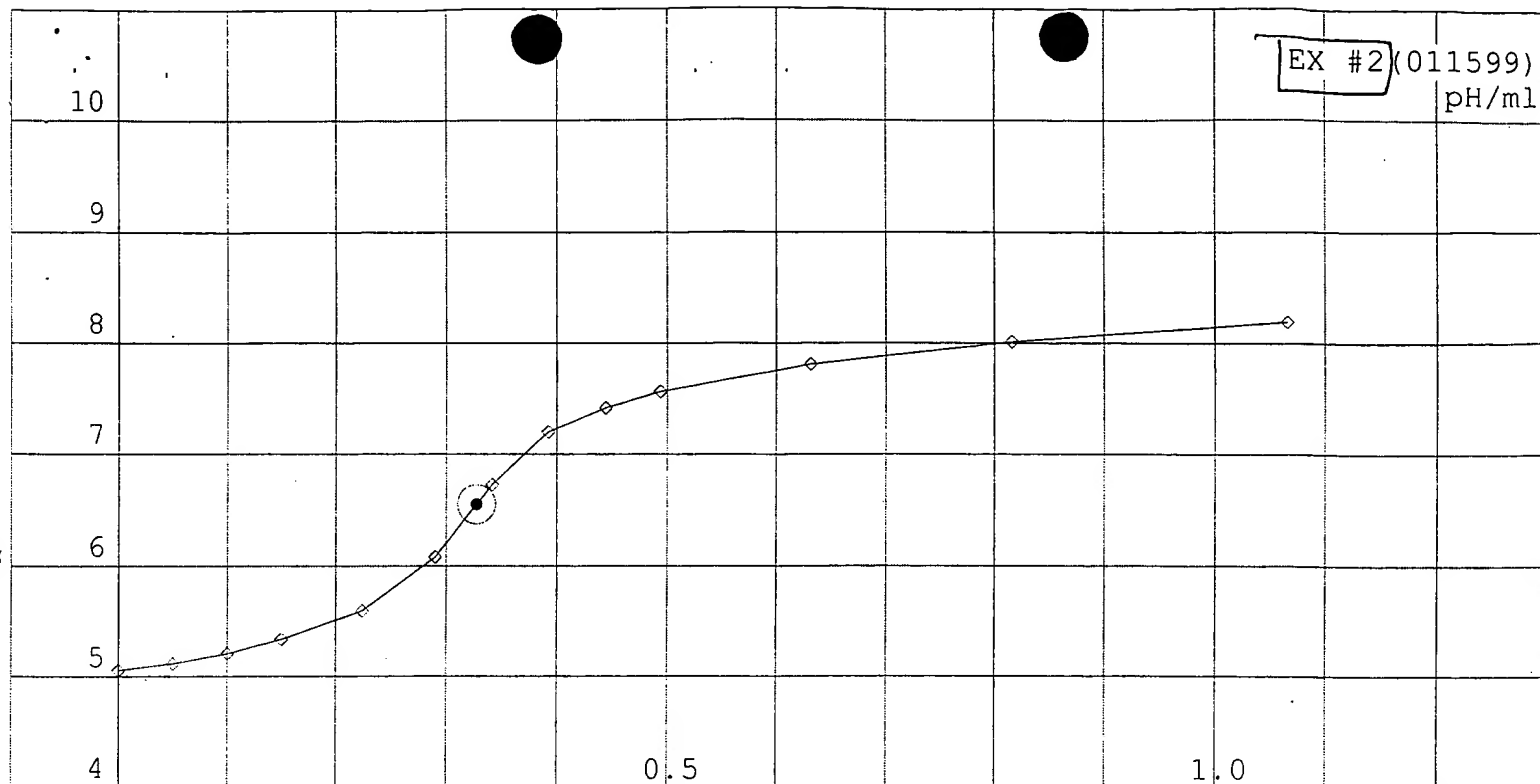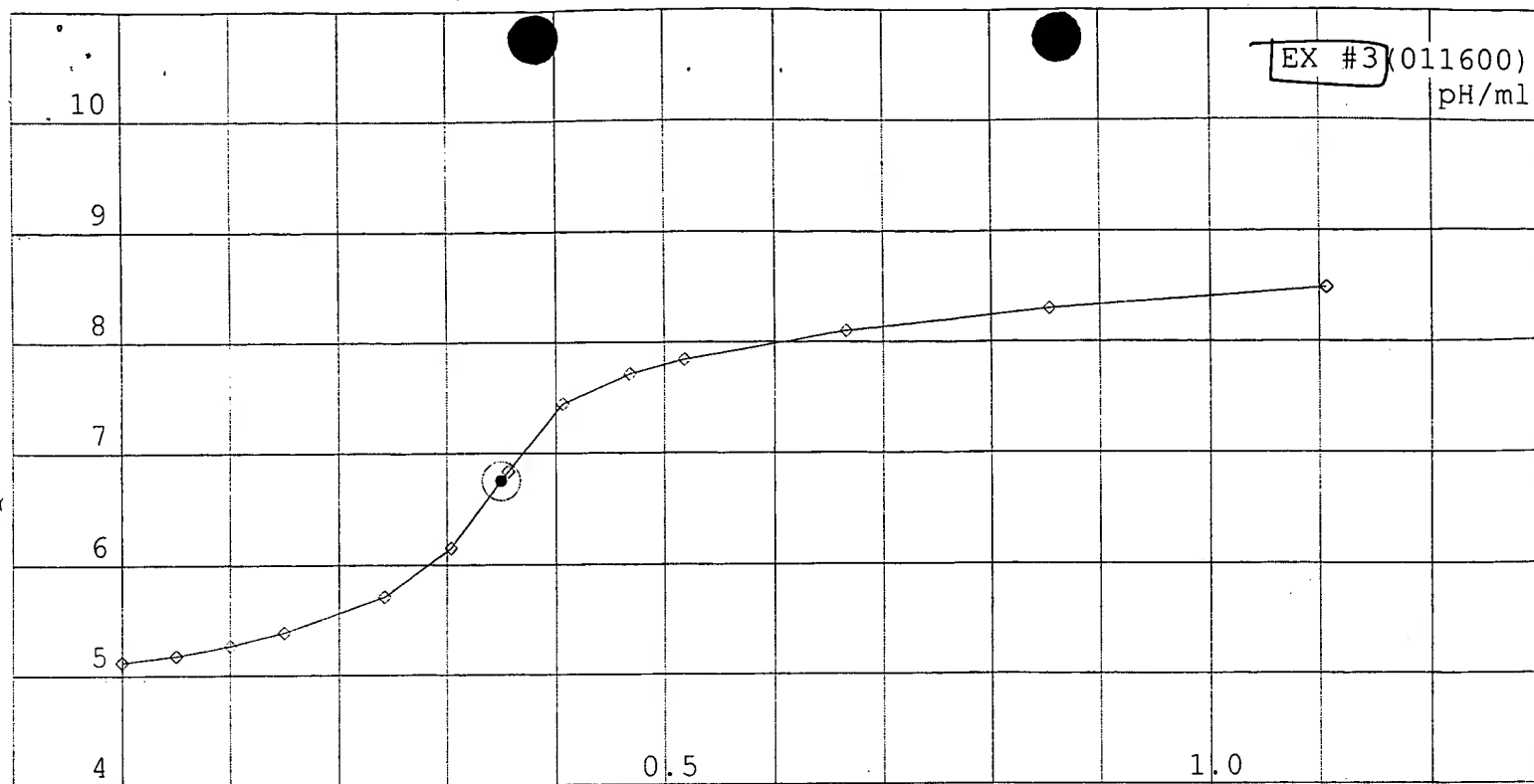
pH

10

9

8

7

6

5

4

0.5   1.0

'fr
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 10:43   216
card label:Appl.751
pH(init)   5.05   DET pH   NE14PA
smpl size   0.5713   id#1   EX #2
EP1   0.328 ml   6.55
stop #EP reached
device label   Titrino   sign:JE
            =============

titront: 0.1N KOH

'mp
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 10:43   216
pH(init)   5.05   DET pH   NE14PA
smpl size   0.5713   id#1   EX #2
 V/ml   pH   T/øC   ERC
 0.0000   5.055   0.0
 0.0500   5.118   34.1
 0.1000   5.209   44.0
 0.1500   5.337   53.5
 0.2240   5.596   63.2
 0.2900   6.082   68.3
 0.3420   6.728   68.9
 0.3920   7.198   65.4
 0.4440   7.416   56.9
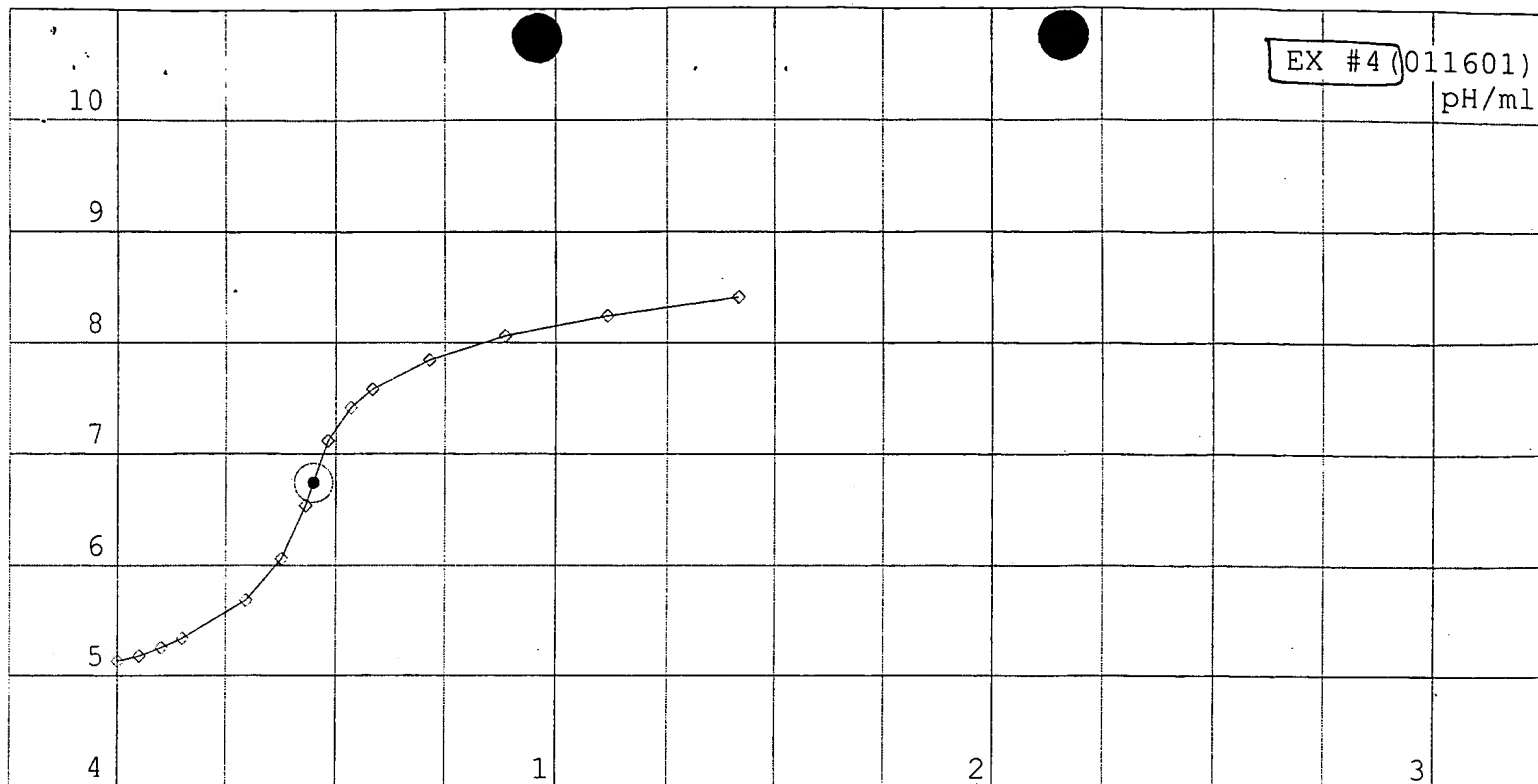 0.4940   7.560   45.8
 0.6320   7.809   35.0
 0.8160   8.011   0.0
 1.0660   8.195   0.0
            =============

pH

10			●			●	
9							
8							
7							
6							
5							
4			0.5			1.0	

'fr
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 10:48   217
card label:Appl.751
pH(init)   5.12   DET pH   NE14PA
smpl size   0.5739   id#1   EX #3
EP1   0.350 ml   6.75
stop #EP reached
device label   Titrino   sign: JE
            ============

'mp
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 10:48   217
pH(init)   5.12   DET pH   NE14PA
smpl size   0.5739   id#1   EX #3

V/ml	pH	T/øC	ERC
0.0000	5.121		0.0
0.0500	5.178		33.1
0.1000	5.270		43.2
0.1500	5.388		52.9
0.2420	5.714		63.1
0.3040	6.151		68.8
0.3560	6.832		70.1
0.4060	7.444		67.2
0.4680	7.712		58.1
0.5180	7.842		44.6
0.6660	8.099		33.9
0.8540	8.301		0.0
1.1060	8.489		0.0

            ============

titrant: 0.1N KOH

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'fr
751 GPD Titrino          09140    751.0020        titrant: 0.1N KOH
date  2001-03-21    time  10:54         218
card label:Appl.751
pH(init)          5.13      DET pH       NE14PA
smpl size     0.5613          id#1       EX #4
EP1        0.450 ml                        6.74
stop #EP reached
device label      Titrino          sign: JE
           =============
'mp
751 GPD Titrino          09140    751.0020
date  2001-03-21    time  10:54         218
pH(init)          5.13      DET pH       NE14PA
smpl size     0.5613          id#1       EX #4
  V/ml                pH    T/øC        ERC
 0.0000             5.131               0.0
 0.0500             5.179              28.2
 0.1000             5.253              36.3
 0.1500             5.339              44.5
 0.2960             5.684              56.2
 0.3780             6.061              65.0
 0.4320             6.539              68.2
 0.4820             7.116              67.0
 0.5340             7.414              60.8
 0.5840             7.579              49.7
 0.7140             7.843              38.0
 0.8860             8.060              27.5
 1.1160             8.246               0.0
 1.4160             8.415               0.0
           =============
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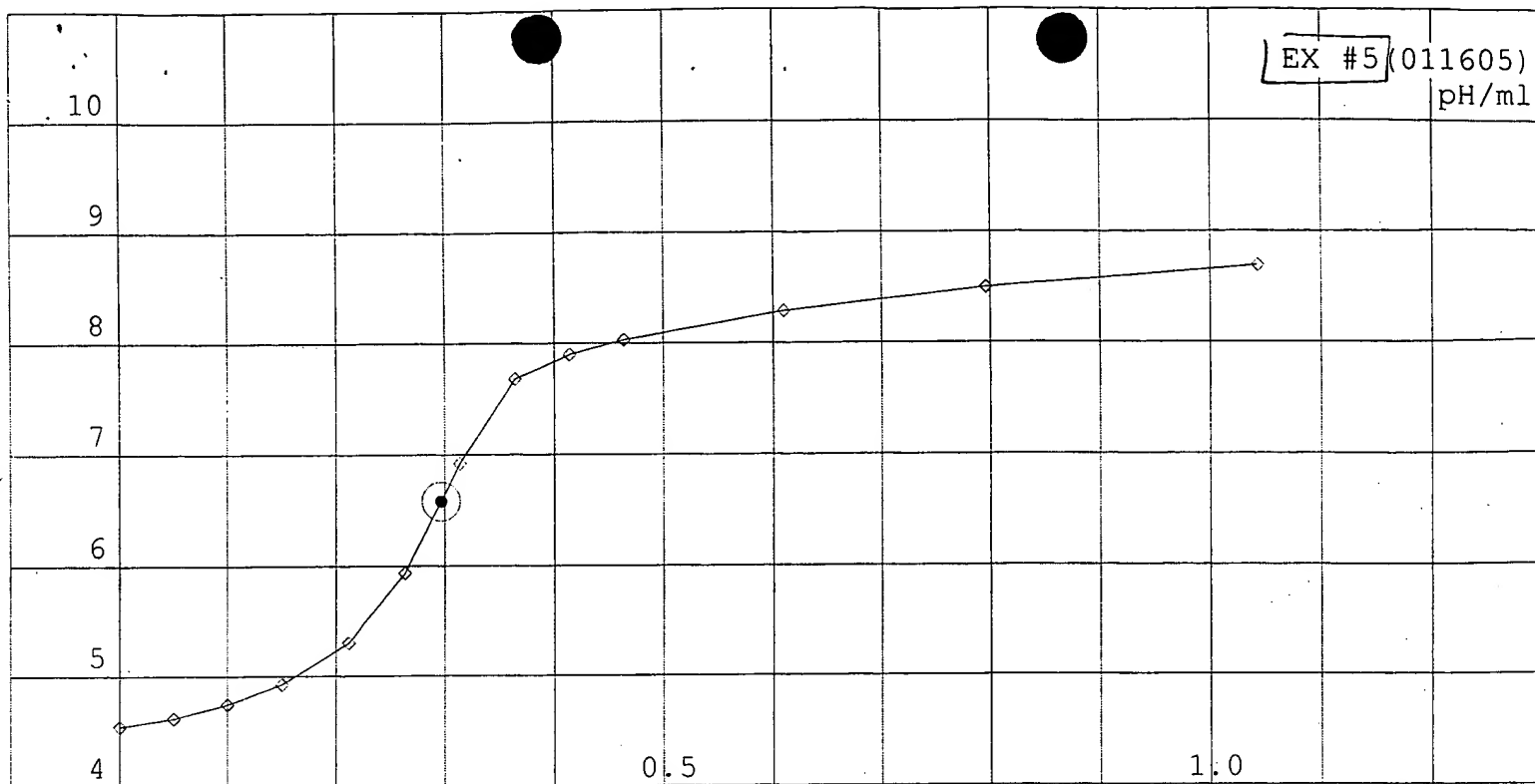
EX #5 (011605)
pH/ml

titranti
0.1N KOH

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'fr
751 GPD Titrino          09140    751.0020
date  2001-03-21    time  13:21        222
card label:Appl.751
pH(init)        4.55     DET pH      NE14PA
smpl size    1.3935          id#1     EX #5
EP1          0.297 ml                   6.58
stop #EP reached
device label     Titrino        sign: JE
              ============

'mp
751 GPD Titrino          09140    751.0020
date  2001-03-21    time  13:21      · 222
pH(init)        4.55     DET pH      NE14PA
smpl size    1.3935          id#1     EX #5
```
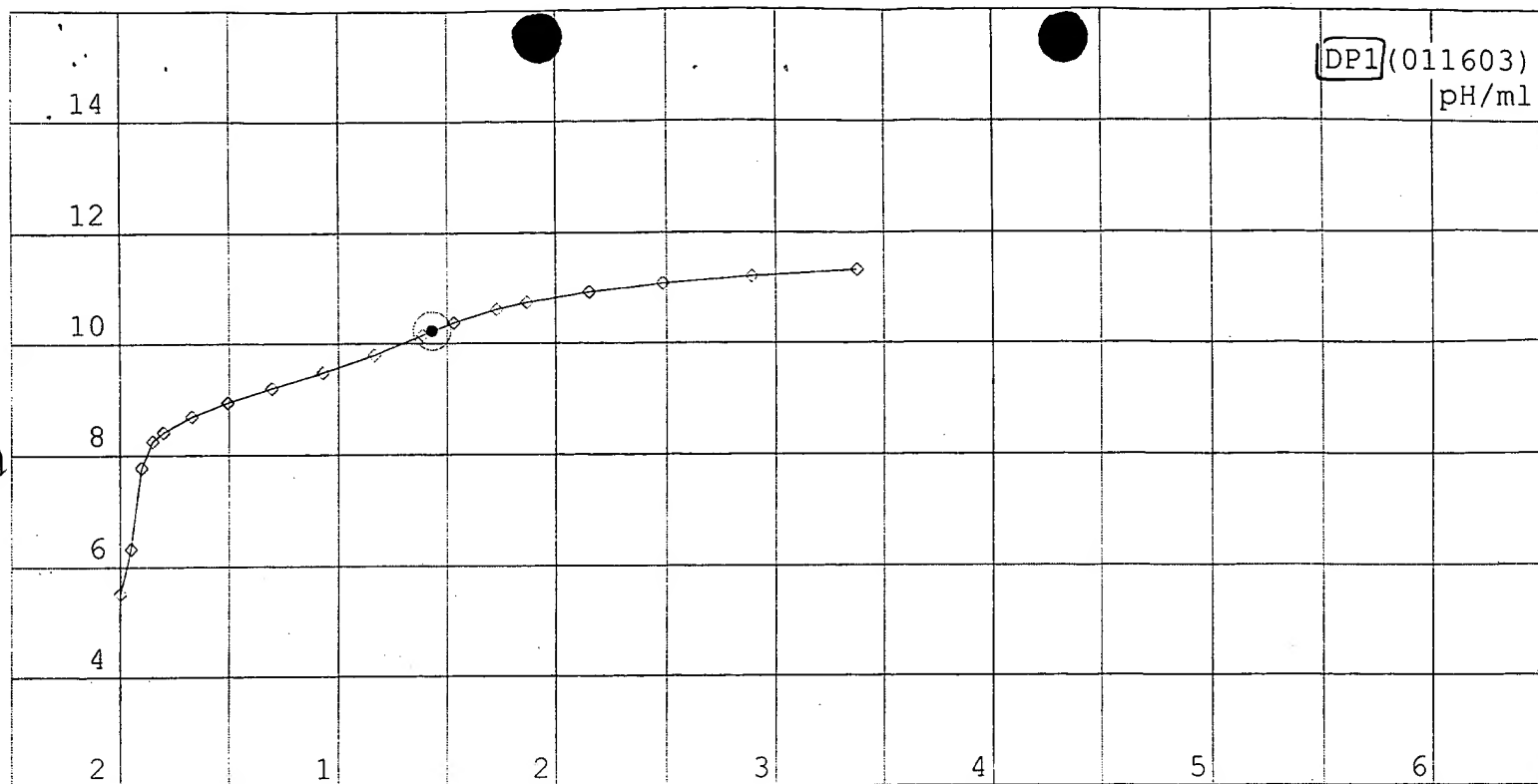
V/ml	pH	T/øC	ERC
0.0000	4.543		0.0
0.0500	4.618		40.7
0.1000	4.743		52.4
0.1500	4.924		62.0
0.2120	5.302		69.1
0.2640	5.936		72.4
0.3140	6.920		72.7
0.3640	7.679		69.4
0.4140	7.898		59.7
0.4640	8.030		45.0
0.6100	8.289		34.6
0.7960	8.496		0.0
1.0440	8.693		0.0

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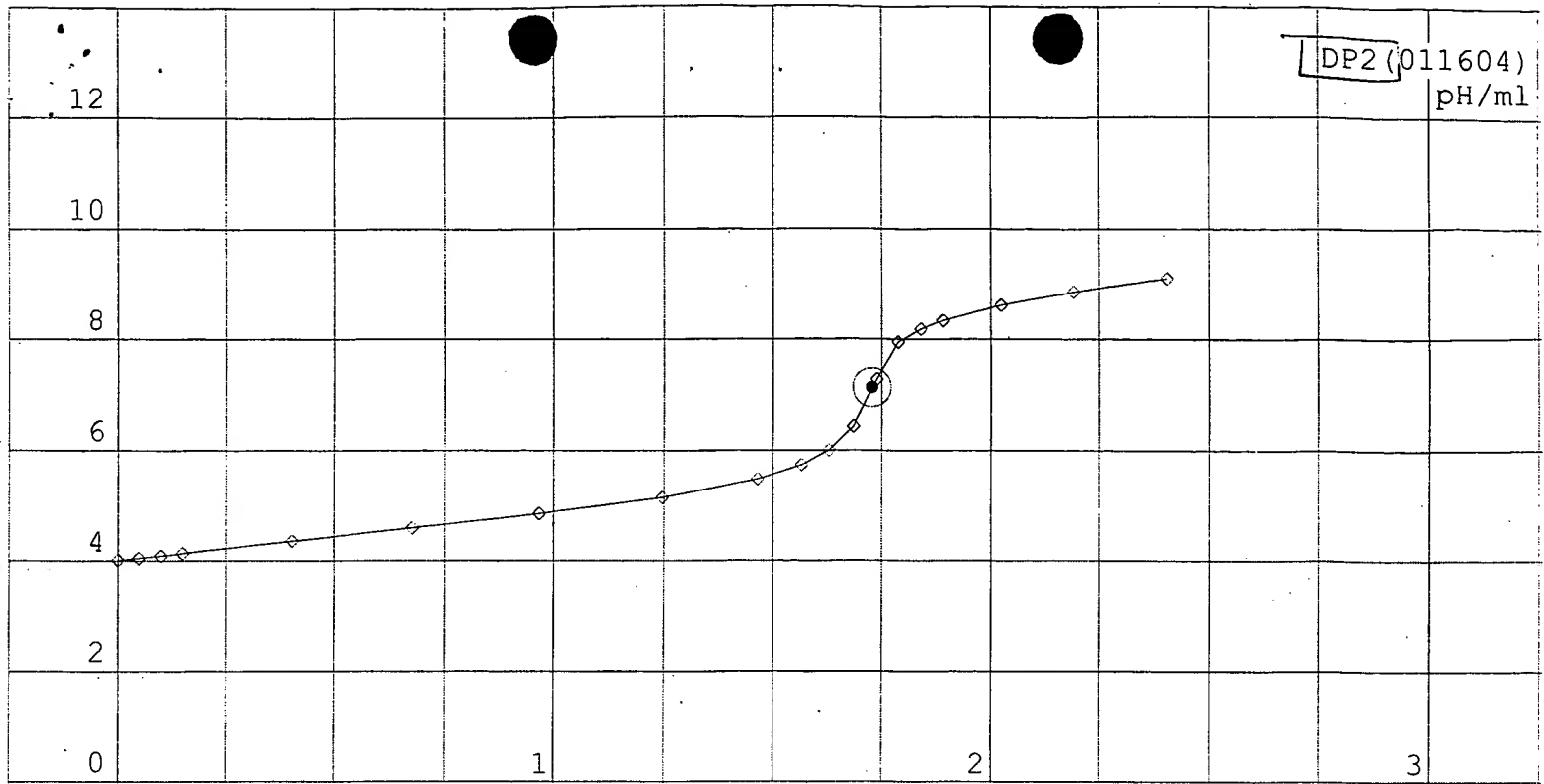'fr
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 11:06   220
card label:Appl.751
pH(init)   5.70   DET pH   NE14PA
smpl size   0.5318   id#1   DP1
EP1   1.432 ml   10.22
stop #EP reached
device label   Titrino   sign:JE
============

titrant: O·1N KOH

'mp
751 GPD Titrino   09140   751.0020
date 2001-03-21   time 11:06   220
pH(init)   5.70   DET pH   NE14PA
smpl size   0.5318   id#1   DP1

V/ml	pH	T/øC	ERC
0.0000	5.519		0.0
0.0500	6.328		73.8
0.1000	7.780		73.3
0.1500	8.243		67.8
0.2000	8.407		53.3
0.3300	8.689		40.7
0.4940	8.940		33.7
0.6980	9.193		30.7
0.9300	9.472		31.3
1.1660	9.791		33.7
1.3860	10.146		34.6
1.5300	10.372		32.2
1.7280	10.619		27.1
1.8660	10.741		21.2
2.1500	10.931		16.0
2.4840	11.083		11.7
2.8920	11.213		0.0
3.3740	11.330		0.0

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pH

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'fr
751 GPD Titrino          09140     751.0020
date  2001-03-21     time  11:12        221          titront: 0.1N KOH
card label:Appl.751
pH(init)       4.01     DET pH      NE14PA
smpl size      0.554        id#1        DP2
EP1            1.728 ml                  7.12
stop #EP reached
device label       Titrino        sign: JE
            =============

'mp
751 GPD Titrino          09140     751.0020
date  2001-03-21     time  11:12        221
pH(init)       4.01     DET pH      NE14PA
smpl size      0.554        id#1        DP2
   V/ml              pH     T/øC       ERC
   0.0000           4.013             0.0
   0.0500           4.046            18.7
   0.1000           4.087            22.6
   0.1500           4.133            23.4
   0.4000           4.356            23.2
   0.6780           4.598            23.5
   0.9640           4.854            26.0
   1.2460           5.147            32.6
   1.4640           5.478            43.2
   1.5660           5.739            54.8
   1.6300           6.004            65.0
   1.6860           6.433            70.3
   1.7380           7.277            71.3
   1.7880           7.945            68.4
   1.8400           8.188            59.9
   1.8900           8.338            48.2
   2.0260           8.628            39.4
   2.1920           8.867             0.0
   2.4040           9.109             0.0

            =============
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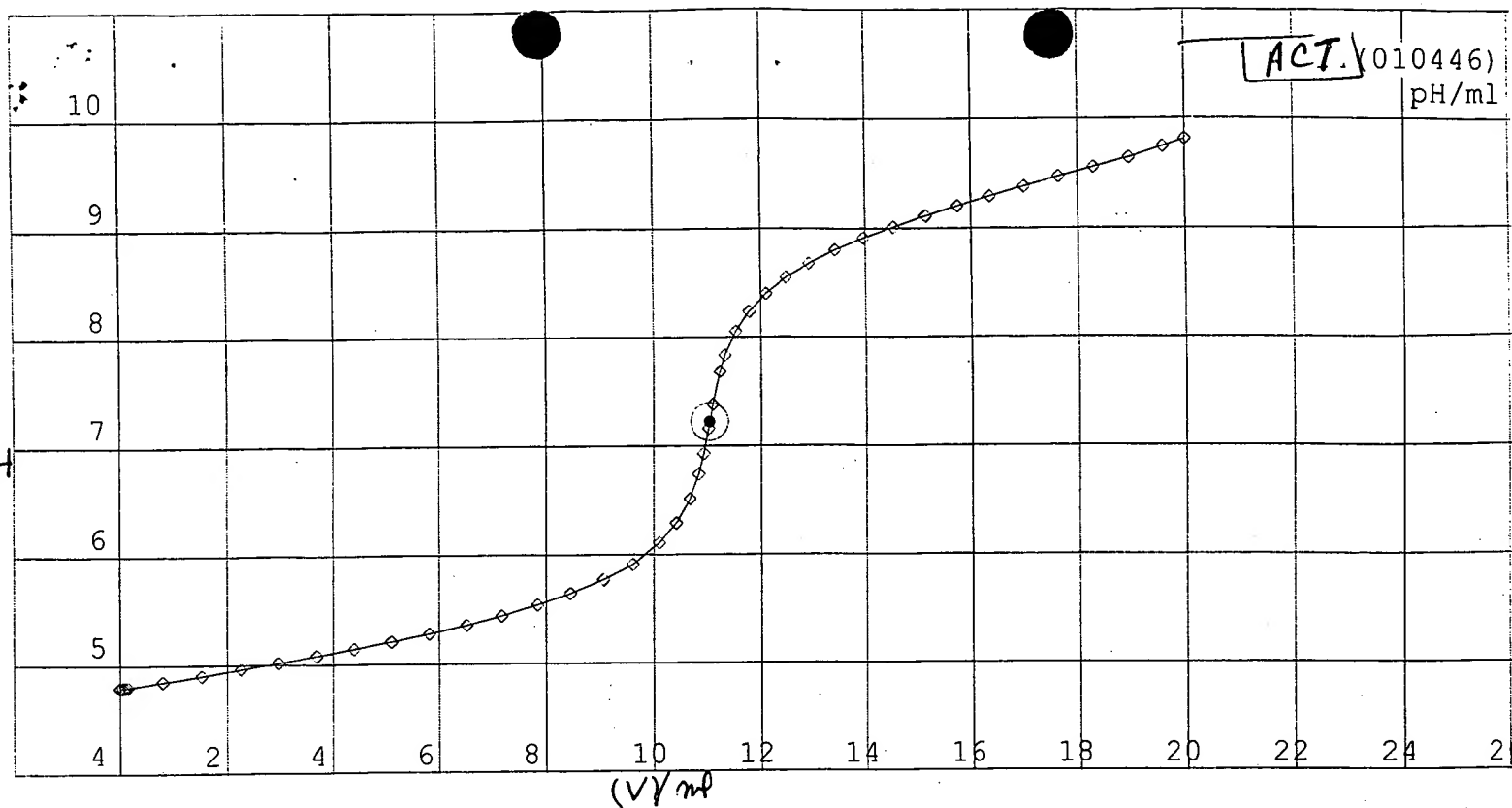
(V)/ml

titrant used: 0.1N KOH

'mp
751 GPD Titrino JE   09140   751.0020
date 2001-02-16   time 10:39   80
pH(init)   4.79   DET pH   NE14
smpl size   0.5549 in   id#1   NE-14
 V/ml ~60ml H2O pH   T/øC   ERC

V/ml	pH	ERC
0.0000	4.792	0.0
0.0500	4.793	1.7
0.1000	4.795	2.4
0.1500	4.799	2.6
0.8100	4.847	2.6
1.5260	4.901	2.6
2.2560	4.961	2.6
2.9740	5.018	2.7
3.6980	5.081	2.8
4.4080	5.144	2.9
5.1160	5.209	3.1
5.8200	5.280	3.4
6.5100	5.360	3.8
7.1760	5.442	4.3
7.8360	5.541	5.0
8.4520	5.645	5.9
9.0540	5.772	7.4
9.5940	5.910	10.1
10.0980	6.110	14.2
10.4200	6.293	20.4
10.6780	6.514	28.7
10.8420	6.744	37.3
10.9360	6.930	43.8
11.0240	7.158	46.8
11.1060	7.382	45.5
11.2400	7.685	40.0
11.3360	7.833	32.1
11.5380	8.052	24.3
11.7900	8.237	17.9
12.1060	8.400	13.4
12.4900	8.549	10.3

12.9320	8.678	8.3
13.4320	8.803	6.9
13.9640	8.911	6.0
14.5360	9.013	5.4
15.1340	9.114	4.9
15.7420	9.205	4.6
16.3700	9.292	4.4
17.0120	9.382	4.3
17.6520	9.470	4.3
18.2940	9.557	4.3
18.9400	9.644	4.5
19.5860	9.743	0.0
20.0000	9.809	0.0

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